Enthalpy and Heat Capacity of Liquid Zirconium

Preliminary Recommendation

The preliminary recommendation for the enthalpy of liquid zirconium is from an assessment by Gurvich et al.[1]. Their enthalpy increments for liquid zirconium relative to the enthalpy of solid zirconium at 298.15 K may be calculated from:

$$H(T,l) - H(298.15K,s) = -16.194 + 0.0426\,T \qquad \textbf{(1)}$$

Enthalpy increments calculated using Eq.(1), shown in Figure 1 and Table 1, are in good agreement with both the 1972 data of Bonnell [2] from 2233 to 3048 K and the more recent Russian data of Kats et al. [3] from 2148 to 2323 K. The enthalpy of liquid zirconium at the zirconium melting point, 2128 $\pm$ 5 K, calculated using Eq.(1) is consistent with the recommended enthalpy of fusion given by the assessment of Gurvich et al.[1], the enthalpy of fusion measured by Korobenko and Savvatimskii [4] using pulse heating, and the enthalpy of fusion obtained from magnetic levitation measurements by Kats et al.[3].

The recommended value for the heat capacity of liquid zirconium is 42.6 $\pm$ 1.8 J mol^{-1} K^{-1}. This value is the value recommended by Gurvich et al. [1] and is equal to the temperature derivative of Eq.(1). It is consistent with the slope of the data of Bonnell [2] and of Kats et al.[3].

Uncertainty

The uncertainty in the values of the enthalpy increments for liquid zirconium calculated using Eq.(1) is $\pm$10%. This uncertainty has been selected to span the range in values obtained by the different equations currently in use in the literature. Figure 1 shows the recommended values for the enthalpy increments of liquid zirconium, the available data, and the 10% uncertainty.

Discussion

The results of measurements of the enthalpy increment for liquid zirconium from 2233 to 2839 K using magnetic levitation in an adiabatic calorimeter, tabulated by Bonnell in his 1972 thesis [2], are given in Table 2. In 1985, Kats et al. [3] published results of their magnetic-levitation measurements of the enthalpy of solid zirconium from 1216 K to the melting point, the enthalpy of liquid zirconium from the melting point to 2323 K, and determination of the enthalpy of fusion. The data of Kats et al. are tabulated in Table 3. Figure 1 shows that the liquid enthalpy increments obtained by Kats et al. are in good agreement with the data of Bonnell.

The paper by Kats et al.[3] is only available in the Russian literature. Therefore, it was not available for the thorough review of zirconium properties published in 1987 by Guillermet [5]. Without the data of Kats et al.[3], there exists no confirmation of the results obtained from the magnetic leviation calorimetry experiments of Bonnell [2]. The value for the enthalpy of fusion obtained by Bonnell, from extrapolation of his liquid enthalpy data, is about 50% lower than values from older drop-calorimetric measurements of Elyutin et al.[6] and values obtained by Martynyuk and Tsapkov [7] from pulse heating experiments. Thus, Guillermet concluded that the enthalpy measurements of Bonnell have a systematic error. Because the slope of the Bonnell data seemed reasonable, Guillermet used it to obtain a constant liquid heat capacity. The recommendations for the enthalpy increments of solid and liquid zirconium given by Guillermet [5] have been recommended by the Scientific Group Thermodata Europe (SGTE) [8] for use in phase diagrams and by Cordfunke and Konings [9]. The values for the enthalpy increments of solid and liquid zirconium determined by Guillermet [5] and recommended by the SGTE [8] are compared with the solid and liquid data of Kats et al. [3] and the liquid data of Bonnell [2] in Figure 2. Figure 2 shows that the enthalpy increments for solid zirconium recommended by Guillermet [5] and the SGTE [8] are consistent with the data of Kats et al. [3] for solid zirconium but the large enthalpy of fusion selected by Guillermet results in enthalpy increments for liquid zirconium that are significantly higher than the experimental data of both Kats et al. [3] and Bonnell [2].

Examination of earlier assessments indicates that the data of Bonnell were not included in either the 1979 JANAF assessment that is given in the 1985 JANAF Thermochemical Tables [10] nor in the 1976 IAEA assessment by Alcock et al. [11]. The values given by Alcock et al. are recommended in the book "Thermochemical Properties of Inorganic Substances by Knacke et al. [12] and in the on-line database of the Russian Academy of Sciences Nuclear Safety Institute (IBRAE). In Figure 3, the data of Kats et al.[3] and of Bonnell [2] are compared with enthalpy increments from the assessment of Gurvich et al.[1], JANAF 1985 [10], Alcock et al.[11], the 1973 edition of Hultgren [13], and the SGTE [8] equation based on the review of Guillermet [5]. Of these various assessments, only the values of Gurvich et al. are consistent with the experimental data. Therefore, the values of Gurvich et al.[1] are recommended.

In Bonnell's levitation calorimetry measurements on four different liquid metals, he found that to quite good precision, the classical theory of a constant heat capacity for the liquid transition metals was obeyed for large temperature spans. Although his zirconium data appeared linear for a temperature range of 700 K above the melting point (2128 to 2839 K), the three data at the highest temperatures appeared to deviate from the linear trend. This deviation could not be attributed to systematic errors because probable systematic errors would lead to deviations in the opposite direction. Both Bonnell [2] and Baykara et al. [14] comment that this deviation could be explained by a temperature dependence in either the heat capacity or the emissivity. Until additional measurements have been made at 2900 K and higher to determine the temperature dependence of the heat capacity and the emissivity, there remains uncertainty in the temperature dependence of the enthalpy and heat capacity of zirconium above 2840 K. Pulse-heating experiments to determine the zirconium enthalpy of fusion and the temperature dependence of the enthalpy, heat capacity and emissivity of liquid zirconium from the melting point to 4000 K are expected to begin in 1998 at the United Institute of High Temperature, Russian Academy of Sciences. This preliminary recommendation will be reassessed when results of these measurements are available.

References

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Figure 1 Recommended Values for the Enthalpy of Liquid Zirconium

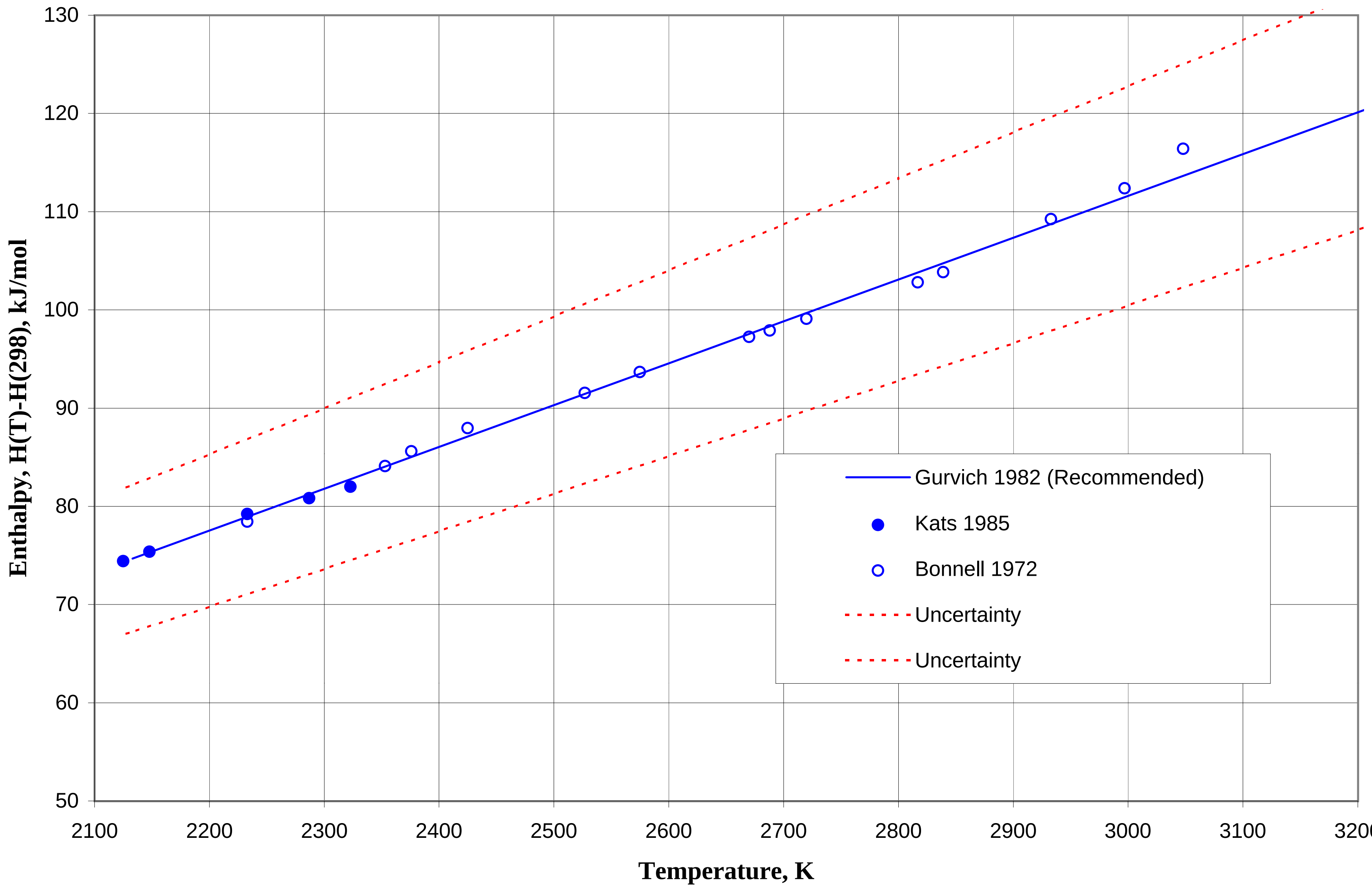

Figure 2 High-Temperature Zirconium Enthalpy

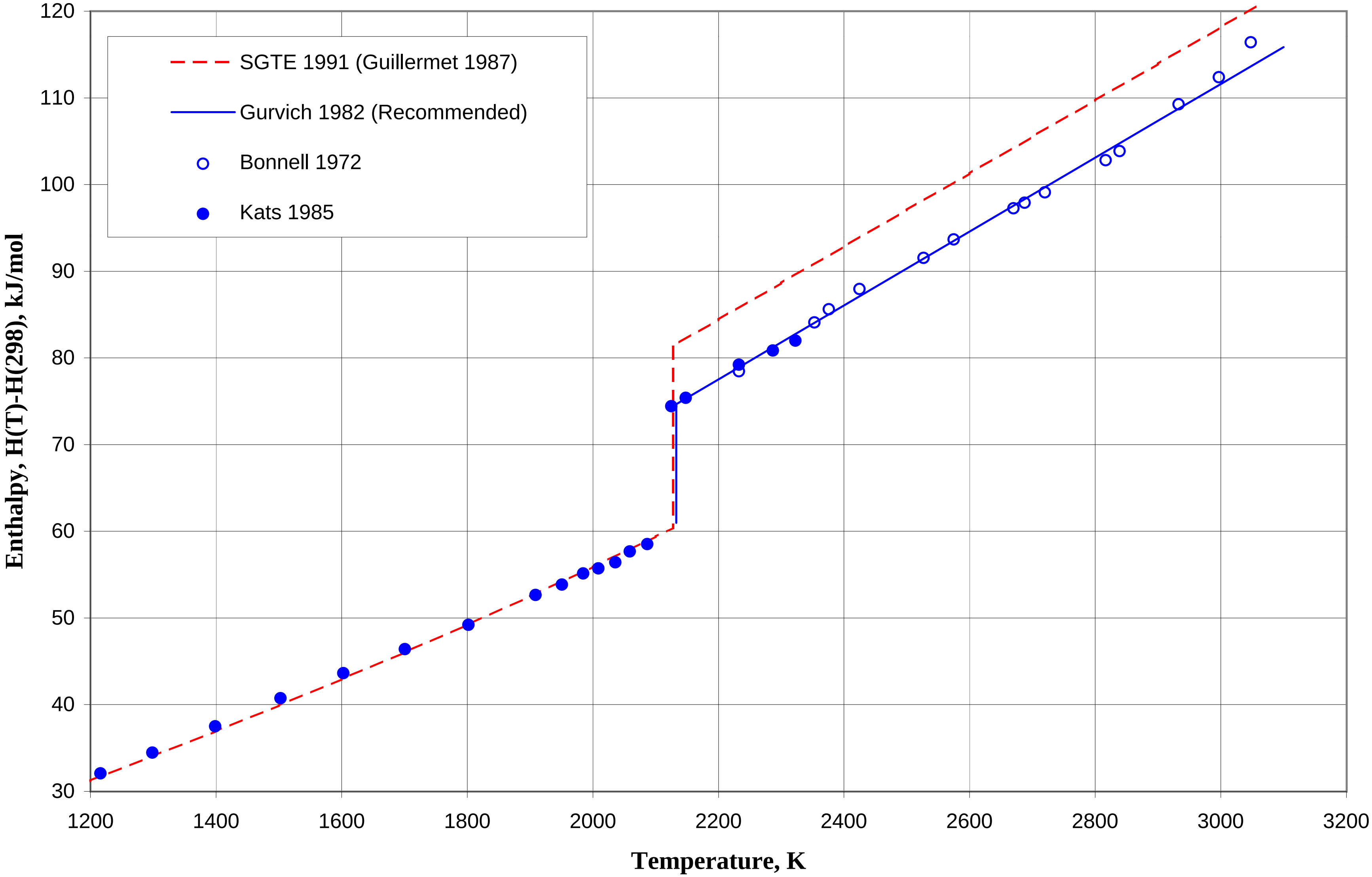

Figure 3 Comparison of Equations for the Enthalpy of Liquid Zirconium

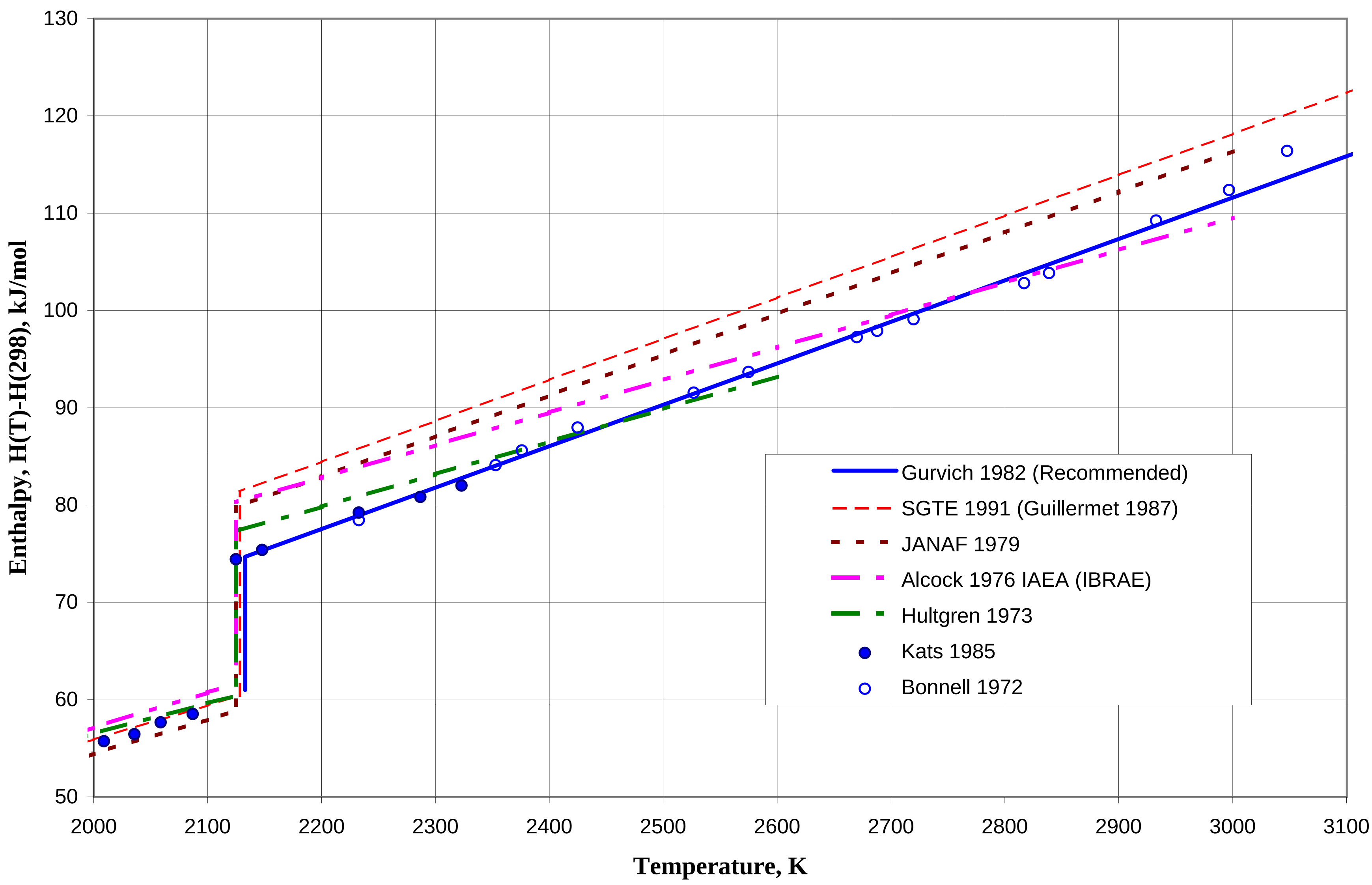

Table 1 Recommended Values for the Enthalpy Increment of Liquid Zirconium.

Temperature, K	Enthalpy H(T) - H(s, 298)
2128	74.5
2200	77.5
2300	81.8
2400	86.0
2500	90.3
2600	94.6
2700	98.8
2800	103.1
2900	107.3
3000	111.6
3100	115.9
3200	120.1
3300	124.4
3400	128.6
3500	132.9
3600	137.2
3700	141.4
3800	145.7
3900	149.9
4000	154.2
4100	158.5
4200	162.7

Table 2 Enthalpy Increments for Liquid Zirconium from Levitation Calorimetry Measurements of Bonnell

Temperature K	H(T) - H(298.15 K) kJ /mole
2233	78.416
2353	84.07
2376	85.57
2425	87.926
2527	91.519
2575	93.648
2670	97.227
2688	97.88
2720	99.078
2817	102.778
2839	103.816
2933	109.222
2997	112.357
3048	116.381

Table 3 Enthalpy Increments for Solid and Liquid Zirconium from Levitation Calorimetry Measurements of Kats et al.

Temperature, K	H(T) - H(298.15 K) kJ /mole
1216	32.05
1299	34.45
1399	37.461
1503	40.718
1603	43.595
1701	46.366
1802	49.172
1909	52.634
1951	53.827
1985	55.101
2009	55.69
2036	56.402
2059	57.632
2087	58.481
2125	74.391
2148	75.356
2233	79.196
2287	80.812
2323	81.972